VARIED MORPHOLOGY CARBON NANOTUBES AND METHOD FOR THEIR MANUFACTURE

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FIELD OF THE INVENTION

The present invention relates generally to carbon nanotubes of varied morphology, and methods for manufacturing carbon nanotubes in large quantities with controlled morphology.

BACKGROUND OF THE INVENTION

Carbon nanotubes (CNTs) offer significant advantages over other materials in that they possess substantially higher strength-to-weight ratio and superior mechanical properties. A major limitation to their large-scale commercialization however, has remained the need for large quantity, cost-effective production methods. Conventional synthetic methods for synthesis of CNTs utilize arc discharge, laser ablation and chemical vapor deposition (CVD).

Existing manufacturing methods using CVD are directed toward obtaining aligned monolayer arrays of CNTs on a catalyst surface that is comprised either of a metallic substrate or a non-metallic substrate whose surface is coated with a metallic material.

Metal catalysts for CNT synthesis disclosed in the prior art involve the deposition of a transition metal catalyst layer as a coating on a substrate by standard methods such as metal vapor deposition and magnetron sputtering. The prior art discloses examples of metallic (non-catalytic) and non-metallic substrates coated with a surface layer of a catalytic metal such as iron by the aforementioned methods. Such processes however, require expensive and complicated apparatus and typically require a high vacuum (10^{-5} to 10^{-7} torr) environment. Furthermore, such methods are only capable of providing a uniform surface layer of the metal catalyst on the substrate on which CNT formation and growth can occur. The surface area of the catalytic metal layer therefore, is substantially similar to that of the substrate on which it is deposited. Since CNT yield is directly related to surface area of the catalytic surface, substantially large areas of metal coated substrate is required to synthesize large quantities of CNTs, which is impractical in terms of existing limitations of the reaction apparatus.

A mesoporous silica sol-gel catalyst impregnated with iron was disclosed by Li et al. [*Science, Vol. 274, (1996), 1701*] for the synthesis of aligned carbon nanotubes. The method described by Li requires the preparation of large, flat surfaces of the iron impregnated mesoporous silica substrates with uniform distribution of pores. According to Li et al., preparation of such large area catalytic substrate is hampered by the inherent tendency to shrink, crack and shatter during their preparation. Meticulous drying procedures therefore, are required to maintain the integrity of the catalyst to obtain large area surfaces, which is

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critical for obtaining high density monolayer CNT arrays. Imperfect catalyst preparation can severely limit yields of CNT product. Also, CNT synthesis by the process of Li et al. requires a reaction temperature of 700°C, which is impractical for substrates such as flat panel glass.

Although such methods are capable of providing highly pure, aligned CNTs, they are not best suited for large-scale production due to low volume (typically several milligrams to grams per batch), low yields based on amount of catalyst and high manufacturing cost. Furthermore, existing methods do not allow control of nanotube morphology, tubule diameter, tubule wall thickness and other structural elements that are important in achieving desired material properties that may required for specific applications. Such drawbacks are limiting factors that restrict the widespread use of CNTs in potential applications.

Most of the prior art methods provide methods for synthesis of linear CNTs without morphology control. However, the anomalous electrical properties exhibited by "kinked" or bent CNT tubules is indicative of the importance of non-linear, branched tubule structures in the development of CNT based electronic devices such as micro-transistors and nanocircuits. Although it is theoretically possible to introduce a wide range of structural defects with useful electronic properties in CNTs, synthetic limitations have precluded such introduction of systematic structural defects. Furthermore, currently available methods do not allow controlled alteration of linear tubule structures during their growth. Post growth modifications of CNTs have been difficult to implement and are prone to uncontrolled and random defects. Li et al disclose a method to synthesize a CNT with a branched Y-junction (*Nature, (1999) Vol. 402, 253-4*) that involves the deposition of carbon onto an thin aluminum sheet wherein Y-shaped molds are etched by an electrochemical process. The

CNTs formed within the aluminum molds are then removed from within the said molds. The branched Y-shaped CNTs obtained by the method however, are not symmetrical with respect to arm length, straightness and angles between arms, since their shape and symmetry is determined by limitations in fabrication of the aluminum mold in which they are formed.

SUMMARY OF THE INVENTION

The present invention provides methods for manufacturing highly pure, non-aligned CNTs by a chemical vapor deposition (CVD) process wherein the nanotube morphology, yield and purity are all controllable by proper choice of optimal process parameters. More specifically, the present invention provides methods for the manufacture of non-aligned CNTs with specific morphologies in high purity, large quantities and high yields. Kilogram quantities of pure product can be synthesized by utilization of the method of the present invention.

The present invention provides CNTs with different types of tubule morphologies that include, for example, (1) cylindrical hollow single-walled or multi-walled nanotube (SWNT and MWNT, respectively) structures, (2) "bamboo-like" structures, wherein successive end-capped graphene layers that are staggered in a telescoping, stacked arrangement, and (3) branched, "Y-shaped" structures with symmetric, straight-armed tubules having fixed angles between arms.

Linear CNTs as defined herein, refers to CNTs that do not contain one or more branches originating from the surface of individual CNT tubules along their linear axes. Branched CNTs as defined herein, refers to non-linear CNTs with at least one location along the linear tubule axis or at the tubule terminal from which one or more tubules originate,

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having linear tubule axes that are non-identical to the tubule from which they originate. Such points of origination of additional tubules (branch points) are also referred to herein as junctions. Branched CNTs include, for example, "Y-shaped" CNTs and "kinked" CNTs.

A key innovation provided by the methods of the present invention is the ability to control the morphology and tubule structural characteristics of CNTs during their formation, thereby enabling the synthesis of CNTs having a specific morphology and structure. In a preferred embodiment, CNTs having either a cylindrical, hollow structure with concentric graphene layers, or a "bamboo-like" structure wherein successive end-capped graphene layers that are staggered in a telescoping, stacked arrangement can be produced. These configurations are schematically illustrated in Figure 1. Control of CNT morphology and tubule structure can be accomplished by varying the parameters of the manufacturing process, for example, by varying the pressure of carbon source/catalyst gas mixture within the CVD reaction chamber, and by the reaction temperature, respectively. The pressure of the carbon source gas/catalyst gas mixture may be low (about 0.001 to 200 torr), moderate (about 200 to 400 torr) or high (about 400 to 760 torr). Depending on the range of gas pressure chosen, CNT morphology can be varied during their formation so as to provide either a single morphology type or a mixture of morphologies. At low gas pressures, cylindrical, completely hollow tubule morphology is obtained, whereas at high pressures, nanotubes with a parabolically shaped (conical), telescoping stacked tubule ("bamboo-like") morphology with capped ends is obtained. A mixture of both tubule morphologies is attainable at the moderate pressure range. Adjustment of reaction temperature in the method of the invention enables control of both individual tubule diameter and the yield the CNT product. The reaction temperatures for synthesizing the CNTs by the present invention

provides a means for controlling structural characteristics of individual tubules such as length, diameter and number of concentric graphene layers. The reaction temperature range for the method of the invention ranges between about 600° and about 1500°C, preferably between about 700°C and about 1200°C. In a preferred embodiment, the reaction temperature ranges between about 750°C and 900°C. Important structural attributes of CNTs that determine their mechanical and electrical properties can be controlled and "tailored" for application specific requirements. Therefore, CNTs of pre-determined morphology and structural attributes can be obtained in high yields (up to 700% based on catalyst substrate weight) by the method of the invention. It will become evident from the embodiments described herein CNTs with precisely controlled morphology and structure can be manufactured by use of optimal process parameters in the method of the invention.

The present invention also provides catalyst materials for the synthesis of CNTs of pre-determined morphologies and methods for utilizing them in the manufacture of varied morphology CNTs. The catalyst material comprises of a catalytic substrate, a catalyst gas, or a combination thereof. For the synthesis of linear CNTs, the catalyst material comprises (1) a catalyst gas, and (2) a catalytic substrate. For the synthesis of branched CNTs, the catalyst material comprises a catalytic substrate either by itself or in combination with a catalyst gas.

In one aspect, the present invention provides micro-particulate, mesoporous catalyst substrates that are used in a process for synthesis of linear CNTs. The catalytic substrate is distributed on the surface of a reaction vessel as a thin layer, following which the reaction vessel containing the catalyst layer is placed in a reaction chamber of a CVD reactor apparatus comprising a heating means to enable chemical vapor deposition of carbon from a carbon source gas. According to the method of the invention, the carbon source gas is mixed

with a catalyst gas in the presence of the catalytic substrate at an elevated temperature. The catalyst gas enables rapid chemical vapor deposition and graphitization of carbon on the catalytic substrate resulting in tubule growth on the surface and within the pores of the said catalytic substrate.

The present invention also provides a catalytic substrate for the synthesis of symmetrical, branched (e.g. Y-shaped) CNTs comprising a transition metal that is supported on a metallic or non-metallic oxide. In one embodiment, the catalytic substrate is distributed on the surface of a reaction vessel as a thin layer. The vessel containing the catalyst layer is then placed in a pyrolytic chamber of a reactor apparatus comprising a heating means that enables deposition of carbon by pyrolysis of a carbon source gas at elevated temperature. The carbon source gas can additionally contain a catalyst gas to enable rapid carbon deposition and CNT growth.

An important innovation of the present invention is the preparation and utilization of different types of catalyst materials for obtaining CNTs of specific morphologies. For synthesis of linear CNTs, a combination catalyst comprising: (1) a catalyst gas and (2) a micro-particulate mesoporous catalytic substrate. The catalyst gas enables the initiation of CNTs at reaction temperatures in a CVD process that are lower (growth initiation begins at about 600°C than those typically required in prior art methods ($\geq$ 700°C). The catalyst gas also facilitates rapid CNT tubule growth compared to known processes. The use of a catalyst gas in the method of the invention therefore, enables CNT growth on substrates with have relatively low strain / melting point such as for example glass substrates used in flat panel display (strain / melting point $\leq$ 666°C). The catalyst gas also provides CNTs with higher

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degree of graphitization that are substantially free of defects, such as those typically caused by entrapment of non-graphitized, amorphous carbon. For synthesis of branched, Y-shaped CNTs, the catalyst substrate comprises at least one transition metal that is supported on a metallic non-metallic oxide. The catalytic metal can be deposited on the metallic non-metallic oxide, which may be in a particulate form. A catalyst gas or gas mixture component can be additionally introduced in the reaction chamber during the synthesis of branched CNTs to enable rapid carbon deposition and CNT growth and provide high graphitization

The catalytic gas component of the catalyst materials can be a substance that is a non-carbon substance that is gaseous at the reaction temperature, and preferably comprises a non-carbon gas such as ammonia, hydrogen, nitrogen, or mixtures thereof. For CVD reaction temperatures less than about 700°C, hydrogen is preferred, while for CVD reaction temperatures greater than about 700°C, the preferred catalyst gas can be ammonia, hydrogen, nitrogen, or a combination thereof. Preferably, the catalyst gas is introduced into the CVD chamber either prior to or simultaneously with the carbon source gas.

The carbon source gas of the invention can be saturated or unsaturated linear hydrocarbons, branched or cyclic hydrocarbon compounds, or mixtures thereof, that are gaseous at the reaction temperature at which they are deposited on the catalytic substrate material. Preferred carbon source gases include methane, propane, acetylene, ethylene, benzene, or mixtures thereof. A currently preferred carbon source gas for the synthesis of linear CNTs is acetylene. For the synthesis of branched CNTs, a currently preferred carbon source gas is methane.

The catalyst substrate component of the invention preferably comprises a micro-particulate, mesoporous sol-gel that is impregnated with nanoparticles of a metal or combination of metals, a metallic alloy, a metal/metallic alloy combination or an organo-metallic compound. The micro-particulate sol-gel may be, for example, mesoporous silica, mesoporous alumina or the like. A combination of sol-gels may also be used as the catalyst substrate component. Useful metals in the catalyst substrate of the invention include transition metals, preferably iron, cobalt, and nickel. Preferred metallic alloys include iron/cobalt, iron/nickel, cobalt/nickel and iron/cobalt nickel. Preferred organometallic compounds are metallocenes, such as for example, ferrocene, nickelocene, or combinations thereof.

The combination catalyst of the present invention comprising a metal impregnated micro-particulate mesoporous catalyst substrate in combination with the catalyst gas provides high yields of CNTs and rapid tubule growth at lower reaction temperatures. Particle sizes of the catalyst substrate material range between about 0.01 and about 100 microns (μM). The catalyst substrate of the present invention provides a catalyst surface area (relative to the of weight of catalyst substrate) that is substantially higher than catalyst substrates in the art and therefore, provides substantially higher yields of surface attached CNT product.

The use of the combination of a catalyst gas and the metal impregnated mesoporous catalyst substrate in the method of the present invention enables formation of carbon nanotubes at lower temperatures (about 600°C) compared to prior art methods. The combination of catalytic materials used in the method of the present invention provides a method of growing carbon nanotubes from a carbon source gas in large quantities with high purity and in high yields. The micro-particulate, mesoporous silica sol-gel catalyst of the

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present invention provides a large surface area for CNT formation and provides that is responsible for the high yields of carbon nanotubes (up to about 700% based on catalyst weight).

In a preferred aspect, the linear CNTs of the present invention are synthesized by CVD deposition of a carbon source gas in a reaction chamber in the presence of a catalyst gas on a metal impregnated, micro-particulate, mesoporous silica sol-gel catalyst at an optimum temperature. The volume ratio of carbon source gas to catalyst gas is maintained between 1:2 to 1:10 and optimum gas pressure is preferably maintained between about 0.1 to about 760 torr at a temperature between about 600° and about 1500°C.

In another preferred aspect, branched (Y-shaped) CNTs are synthesized by pyrolysis of a carbon source gas in a reaction chamber on a catalyst substrate comprising a transition metal deposited on a metal oxide at an optimum temperature that enables the formation of branched (Y-shaped) CNTs on said catalyst substrate. The carbon source gas flow preferably is maintained between about 1 sccm and about 1000 sccm (standard cubic centimeter / minute), and the reaction temperature is preferably maintained between about 600°C and about 1500°C.

A technical advantage of the present invention is that the present methods are designed to produce CNTs with controlled morphology (shape), diameter, wall thickness and length in high yields that can be purified easily by washing with a solvent. Solvents useful for purification of CNTs include inorganic acids, such as for example hydrofluoric acid (HF). Large quantities of highly pure CNTs with pre-determined morphology and high degree of graphitization can be obtained by the process of the invention. The methods of the invention

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provide large quantity, cost efficient synthetic processes for linear and branched CNTs that are suited for a variety of applications such as hydrogen storage, electrochemical capacitors, lithium ion batteries, high efficiency fuel cells, semiconductors, nanoelectronic components and high strength composite materials.

It is an object of the invention to provide carbon nanotubes (CNTs) with different morphologies and structural properties in high purity suited for specific applications.

It is another object of the invention to provide methods for manufacturing CNTs in large quantities and in high yields that are cost-effective and commercially viable.

It is yet another object of the invention to provide a catalyst combination comprising a substrate catalyst material and a catalyst gas that enables production of linear CNTs with different morpholgies in high yields relative to weight of catalyst material, and initiate their growth at moderate temperatures.

It is yet another object of the invention to provide a catalyst material comprising a catalyst material comprising a catalytic substrate that enables production of symmetrically branched (Y-shaped) CNTs in high yields (relative to weight of catalyst material).

It is a further object of the invention to provide a manufacturing process and apparatus for CNTs that may be configured either as a batch process or a continuous process.

The foregoing and other objects, features and advantages of the invention will become more apparent from the following description of the drawings and detailed description of particular embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

The objects and features of the invention can be better understood with reference to the following detailed description and accompanying drawings.

Figure 1 is a schematic drawing illustrating carbon nanotube (CNT) morphologies.

Figure 2 shows low magnification TEM photomicrographs of CNTs grown at gas pressures of (a) 0.6 (b) 50 (c) 200 (d) 400 (e) 600 and (f) 760 torr.

Figure 3 shows high magnification TEM photomicrographs of CNTs grown at gas pressures of (a) 0.6 (b) 200 (c) 400 and (d) 760 torr.

Figure 4 shows schematic drawing of proposed mechanism of CNT growth at different gas pressures.

Figure 5 shows a schematic illustration of the manufacturing apparatus and set up for CNT synthesis.

Figure 6 shows yield of CNTs (as a weight ratio of CNTs to catalyst substrate) as a function of different gas pressures. Inset shows CNT yield with reaction time.

Figure 7 shows SEM photomicrographs of CNTs grown at gas pressures of (a) 0.6 (b) 50 (c) 200 (d) 400 (e) 600 and (f) 760 torr.

Figure 8 shows low magnification TEM photomicrographs of "bamboo-like" CNTs synthesized at (a) 800°C (b) 950°C and (c) 1050°C.

Figure 9 shows tubule diameter dependence on compartmental density of "bamboo-like" CNTs synthesized at 800°C.

Figure 10 shows high-resolution TEM photomicrographs of "bamboo-like" CNTs synthesized at (a) 650°C (b) 800°C and (c) 1050°C.

Figure 11 shows SEM photomicrograhs of symmetrically branched (Y-shaped) CNTs at (a) low magnification (scale bar = 1µm) and (b) high magnification (scale bar = 200 nm).

Figure 12 shows TEM photomicrographs branched CNT Y-junctions with (a) straight hollow arms and uniform diameter (scale bar = 100 nm) (b) pear-shaped particle cap at tubule terminal (scale bar = 100 nm) [expanded in bottom inset] and XDS photomicrograph (top right inset) showing composition of particle (c) a branched CNT with a double Y-junction (scale bar = 100 nm) [open tubule shown in inset] and (d) high resolution partial image of a well graphitized, hollow tubule Y-junction.

DETAILED DESCRIPTION OF THE INVENTION

In one aspect, the present invention relates to a material comprising a substrate containing one or more linear carbon nanotubes (CNTs) of pre-determined morphology originating from the surface of said substrate. The morphology of tubules of the CNTs can be cylindrical with a hollow core, or stacked conical segments with capped ends ("bamboo-like"). A mixture of both morphologies can be obtained by varying the appropriate reaction parameters that are described herein

In a preferred embodiment, the materials containing the linear CNTs of the present invention include (1) a micro-particulate, mesoporous catalyst substrate with particle size ranging from about 0.1 μm to about 100 μm (2) a plurality of free standing, linearly extending carbon nanotubes originating from and attached to the substrate surface, and extending outwardly from the substrate outer surface, and (3) one or more carbon nanotubes with a morphology that is either hollow core tubular configuration, or an end capped stacked conical ("bamboo-like") configuration, both morphological forms being comprised of either a single or multiple layers of graphitized carbon. The invention further comprises methods for manufacturing the materials.

In another preferred embodiment, materials containing the CNTs of the invention include at least one transition metal deposited on or impregnated within a metallic or non-metallic oxide. The said metallic or non-metallic oxide can be particulate, e.g., in a macro-particulate form (average diameter ranging from about 1mm to about 1000mm), and most preferably, in a micro-particulate form (average diameter ranging from about 0.01 to about 1000 μm).

In yet another preferred embodiment, the CNTs of the present invention are separated from the substrate material and exist in a free standing, unsupported form.

Referring to Figure 1, linear CNTs manufactured by the method of the present invention are non-aligned, substantially linear, concentric tubules with hollow cores, or capped conical tubules stacked in a bamboo-like arrangement. The nanotube morphology may be controlled by choosing the appropriate catalyst material and reaction conditions in the synthetic method of the present inventions as detailed below in different embodiments.

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Depending on choice of such conditions, large quantities (kilogram scale) of highly pure carbon nanotubes of desired morphology that are substantially free of impurity based defects (occurring from entrapment of amorphous carbon or catalyst particles) can be obtained in high yields.

The linear CNTs obtained by the present invention have diameters ranging from about 0.7 to about 200 nanometers (nm) and are comprised of a single or a plurality of concentric graphene layers (graphitized carbon). The nanotube diameter and graphene layer arrangement may be controlled by optimization of reaction temperature during their synthesis. Thus the method of the present invention allows the synthesis of carbon nanotubes with defined tubule diameters and desired layered structure.

Referring to Figure 2, low magnification TEM images of linear CNTs grown at low, intermediate and high gas pressures indicate that the tubule morphology may be controllably changed by choice of gas pressure. CNTs grown at a gas pressure of 0.6 torr (Fig. 2a) predominantly have a morphology that consists of a tubular configuration, completely hollow cores, small diameter, and a smooth surface. At 50 torr, morphology is essentially similar to that at 0.6 torr, except that a small amount of tubules have an end capped conically shaped stacked configuration ("bamboo-like") (Fig. 2b). At a gas pressure of 200 torr, the morphology of the CNTs are predominantly the end- capped, conical stacked configuration ("bamboo-like") regardless of their outer diameters and wall thickness. The density of the compartments within individual tubules of the CNTs is high, with inter-compartmental distance inside these "bamboo-like" structures ranging from 25 to 80 nm (Fig. 2c). At gas pressures greater than 200 torr, an entirely "bamboo-like" morphology is obtained for the CNTs, with increased compartmental density. The inter-compartmental distances within the

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individual CNTs decrease with increasing gas pressure (10-50 nm at 400 torr and 10-40 nm at 600 and 760 torr respectively). CNTs synthesized at 760 torr have a wider tubule diameter (20 nm to 55 nm (Fig. 2f), have thin walls and smooth surfaces.

In comparison to linear CNTs synthesized at a gas pressure of 200 torr, those synthesized at higher pressures (400 and 600 torr) are highly curved and have broken ends (Figs. 2d and 2e). This is attributed to fracturing of the CNTs during the TEM specimen preparation, which is indicative that CNTs with a "bamboo-like" morphology may be readily cleaved into shorter sections compared to the tubular type.

Prerequisites for superior mechanical properties in CNTs include complete formation of crystalline graphene layers (graphitization) and formation of multiple concentric layers within each tubule and a hollow core, with minimal defects such as those typically caused by entrapment of non-graphitized (amorphous) carbon and metal catalyst particles. Referring to in Figure 3, which shows TEM photomicrographs detailing morphologies of linear CNTs grown at different gas pressures, it is seen that CNTs grown at pressures between 0.6 to 200 torr have good graphitization, their walls comprising of about 10 graphene layers all of which terminate at the end of the CNT that is distal from the substrate (i.e. the fringes are parallel to the axis of the CNT), and possess completely hollow cores.

Linear CNTs grown at 200 torr have good graphitization, with walls comprised of about 15 graphene layers. The individual tubules are "bamboo-like" rather than completely hollow, with diaphragms that containing low number of graphene layers ($\leq$ 5 layers). All the graphene layers terminate at the surface of the CNTs, and the angle between the fringes of the wall and the axis of the CNT (the inclination angle) is about 3° (Fig. 3b).

Linear CNTs grown at intermediate gas pressures (400 - 600 torr) have a "bamboo-like" structure, more of graphene layers in the walls and diaphragms of tubules (typically 25 and 10 graphene layers in their walls and diaphragms, respectively (Fig. 3c)), but less graphitization (lower crystallinity) due to a faster growth rate. Despite the low crystallinity, all graphene layers terminate on the tubule surface with inclination angle of about 6°. CNTs grown at 760 torr have higher graphitization than those grown at 400-600 torr, have a "bamboo-like" structural morphology consisting of parabolic-shaped layers stacked regularly along their symmetric axes (Fig. 3d). All the graphene layers terminate within a short length along growth direction on the surface of the CNTs resulting in a high density of exposed edges for individual layers. The inclination angle of the fringes on the wall of the CNTs is about 13 °(Fig. 3d). The high number of terminal carbon atoms on the tubule surface is expected to impart differentiated chemical and mechanical properties in these CNTs compared the hollow, tubular type, and render them more amenable for attachment of organic molecules.

The methods of the invention enables alteration of linear CNT morphology by controlling gas pressure. At low pressures, CNTs with a tubular hollow structure can be obtained, while at high pressure, CNTs with "bamboo-like" structure and increased compartmental density can be obtained. The number of graphene layers, which is related to thickness of the tubule wall and diaphragm of the CNTs, also can be controlled during their formation by control of gas pressure. Once the first layer forms in bamboo-like structure, all subsequent layers will terminate on the surface of the CNT.

The growth mechanism for linear CNTs obtained by the method of the invention shows that they grow outward from the both the surface and from within the pores of the

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mesoporous catalyst substrate. Carbon atoms dissolve into catalyst droplets, diffuse through the catalytic particle and precipitate on the other side of the catalyst droplet to form CNTs. Based on this mechanism, the effect of growth rate and CNT tubule morphology on gas pressure is illustrated in Figure 4. Two different carbon atom precipitation areas on the iron catalyst particle (Fe) are indicated with letters A and B (Fig. 4a). Assuming that all acetylene molecules of the carbon source gas can decompose into carbon atoms involved in CNT growth, variation of reaction gas pressure will result in a change in carbon atom concentration, which, in turn, influences the manner in which CNTs grow. At low pressure, when concentration of the carbon atoms is low and dissolution and diffusion are limited, carbon atoms dissolved into the catalyst particles prefer to diffuse towards area A rather than the distant, opposite area B. The carbon atoms precipitated in area A form completely hollow CNTs (Fig. 4b). Due to the low concentration of the carbon atoms, the growth rate of CNTs is suppressed, so the yield is relatively low. At high reaction gas pressure, the concentration of carbon atoms increases, the dissolution rate of carbon atoms into the catalyst particles increases, resulting in an increase in the concentration of carbon atoms dissolved inside the catalyst particles. The enriched carbon atoms can diffuse towards both area A and area B on the catalyst particles, then the carbon atoms precipitate to form dome-like carbon shell (Fig. 4c; for simplification only one graphene layer is shown). However, due to the low concentration of carbon atoms and the steric characteristic of the catalyst particles the diffuse rates towards area A is greater than that towards area B. The precipitation rates of carbon atoms at area A is therefore, faster than in area B. Consequently, a concentric graphene layer with closed cap and defined length forms (Fig. 4d). Subsequently, a second dome-like carbon shell forms in a similar manner. This process is repetitive and results in multiple

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analogous capped graphene layers which are separated by a fixed distance along the direction of tubule growth (growth axis), whereby a "bamboo-like" CNT with uniform density of compartments is obtained (Fig. 4e). The concentric graphene layers have a relatively larger diameter at the growth ends than at the capped ends. While the diameters at the capped ends are fixed after their formation, the diameters at the open growth ends continue to increase with continued tubule growth. Once the larger open end diameter of a graphene layer exceeds the carbon precipitation area A on the catalyst particle, the layer stops growing due to non-availability of carbon atoms, and leaves its edge on the surface of CNTs (Fig. 4f). As this process continues, all the initial inner layers shift out, in turn, to the surface then terminate in a regular manner. At high carbon atom concentrations obtained at high reaction gas pressure, the dissolution, diffusion and precipitation rates of carbon atoms increase substantially. As a result, a plurality of graphene layers precipitate simultaneously to form a multi-layered diaphragm in the "bamboo-like" CNT. CNTs grown at a high precipitation rate of carbon atoms therefore, have high compartmental density, which is indicative of the graphene layers being shifted out to the surface at a high rate. As a result, the graphene layer edges exposed on the surface of the CNTs also have a high density and a high inclination angle with reference to the CNT axis.

The catalyst material used in the present invention for synthesis of linear CNTs comprises 1) a catalyst gas that may be combined with a carbon source gas that is deposited on a substrate surface by chemical vapor deposition (CVD) and 2) a metallic, metal alloy an organometallic material or a combination thereof, that is impregnated or deposited on the surface and within the pores of a micro-particulate, mesoporous silica or alumina sol-gel.

The catalyst gas component of the catalyst material preferably is a non-carbon gas such as ammonia, hydrogen, nitrogen, or a mixture thereof. For CVD reaction temperatures less than about 700°C hydrogen is the preferred catalyst gas, while for CVD reaction temperatures greater than about 700°C, the catalyst gas preferably is ammonia, hydrogen, nitrogen or a combination thereof. Preferably, the catalyst gas is introduced into the CVD chamber either prior to or simultaneously with the carbon source gas. The nanotube nucleation process on the catalyst substrate is catalyzed by the catalyst gas, which enables every metal catalyst cap within individual tubules to catalyze the efficient and rapid growth of CNTs.

The carbon source gas preferably consists of unsaturated linear hydrocarbons, branched or cyclic hydrocarbon compounds, or mixtures thereof, that are gaseous at the reaction temperature at which they are deposited on the catalytic substrate material. Preferred carbon source gases include methane, propane, acetylene, ethylene, benzene, or mixtures thereof. A currently preferred carbon source gas for the synthesis of linear CNTs is acetylene. For the synthesis of branched CNTs, a currently preferred carbon source gas is methane.

The catalytic substrate component of the catalyst material for synthesis of linear CNTs of the invention preferably comprises metallic particles (preferably nanoparticles), an organo-metallic material, or combinations thereof that are impregnated in a micro-particulate mesoporous sol gel. The metallic material comprises at least a transition metal, a metal alloy or mixtures thereof. The organometallic material comprises at least one transition metal-containing compound such as for example, ferrocene or nickelocene. The organometallic material can be also combined with an organic compound, such as for example a

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combination of nickelocene and thiophene. Preferred metallic nanoparticles are transition

metals, such as for example, iron, cobalt, nickel, metal alloys such as for example iron/cobalt,

cobalt/nickel, iron/nickel, iron/cobalt/nickel , or combinations thereof.

The micro-particulate sol-gel of the invention may be, for example, mesoporous

silica, mesoporous alumina or the like. A combination of sol-gels may also be used as the

catalyst substrate component.

In a preferred embodiment, the catalytic substrate comprises iron nanoparticles that

are impregnated in mesoporous silica, which is ground into micro-particles to increase

reactive surface area of the catalyst substrate. In a preferred embodiment, the particle size of

the catalyst substrate ranges from about 0.1 to about 100 μm.

Production of linear CNT materials of the present invention is accomplished by

distribution of micro-particulate catalyst substrate on the surface of an open container (boat),

which is then placed into the reaction chamber of a CVD apparatus and exposed to a flow of

a gas mixture containing the carbon source gas and catalyst gas. The reaction temperature,

gas pressure and reaction time are maintained under pre-determined conditions effective to

cause formation and growth of a plurality of carbon nanotubes on the catalyst substrate

surface. The CVD chamber temperature and gas pressure are optimized to control and obtain

the desired the morphology of carbon nanotubes during their growth.

Figure 5 shows a schematic illustration of a preferred manufacturing apparatus and

set up for CNT production by the method of the invention. A reaction chamber 1 has an

internal volume capable of accommodating sample boat 2 that is capable of containing the

catalyst material for CNT growth. Chamber 2 comprises a heater 3 controlled by a controller

4 that enables the reaction temperature inside chamber 2 to be maintained at a level so as to

enable initiation of CNT growth. The flow rate of the carbon source gas and catalyst gas mixture 6 into chamber 2 is controlled by a mass flow controller 5. Pressure transducer 7 enables monitoring of gas pressure inside chamber 2 which is controlled by valve 9 that is operated by valve controller 8. Vacuum pump 10 is capable of evacuating and maintaining the appropriate pressure inside chamber 2.

The methods of the present invention provide high yields of linear CNTs relative to those obtained by conventional processes known in the art. Yields of up to about 700% based on weight of catalyst substrate are achievable. In one embodiment of the invention, the yield (weight ratio of CNTs to the iron embedded silica) of CNTs from silica powder is optimized by maintaining optimum gas pressure and reaction temperature in the chamber during the growth. The effect dependence of gas pressure on CNT yield is shown in Figure 6. The relative yield (based on weight of catalyst substrate) is lower at low and high gas pressures, and is highest at intermediate pressure. The relative yields at 0.6, 50, 200, 400, 600 and 760 torr are 143%, 153%, 486%, 592%, 633% and 355%, respectively.

The reaction time for linear CNT formation may be optimized in the method of the present invention at the optimized gas pressure to obtain high yields of product. Figure 6 (inset) shows the effect of reaction time on CNT yield. By varying the reaction time from 2 to 24 hours at 0.6 torr the relative yield increases by 25% at 5 hours and 43% at 12 hours. Further increase in reaction time does not result in a substantial increase in yield. Thus an optimal relative yield of 200% can be achieved for a reaction time of 12 hours at 0.6 torr.

The ability to vary the gas pressure in the method of the present invention provides a means to control of linear CNT tube diameter size and uniformity during their formation. Figure 7 shows scanning electron microscopy (SEM) photomicrographs of the CNTs grown

at different pressures of 0.6, 50, 200, 400, 600 and 760 torr respectively. CNTs grown at 0.6

and 50 torr have small diameters that are distributed over a narrow range, smooth surfaces

and a tubule length of about 10 to 20 μm (Figs. 7a and 7b). At 200 torr, a fraction of CNTs

with a larger, non-uniform diameters with a smooth surface are observed (Fig. 7c). CNTs

grown at 400 and 600 torr have large, uniform diameters, increased surface roughness, and

exhibit high curvature and are of shorter length (Figs. 7d and 7e). At gas pressures above

760 torr, the CNT diameters are non-uniform (Fig. 7f) and similar to those obtained at 200

torr. The tubule surface is however, smooth. When observed under SEM under identical

conditions, photomicrographs obtained for CNTs synthesized below 200 torr are much

clearer than those synthesized above 400 torr. This observation, combined with the

difference in morphologies, is indicative of micro-structural differences between these CNTs

obtained at different pressures. SEM photomicrographs indicate that CNTs synthesized at all

pressures have a high degree of purity.

The yield of linear CNTs changes with reaction temperature in the method of the

invention. Table 1 shows the dependence CNT yield on reaction (growth) temperature. It is

evident from the table that yield is highest at intermediate reaction temperatures and reaches

a maximum of about 700 weight % (relative to weight of substrate catalyst). The yields

listed in Table 1 were calculation of CNTs obtained by mechanically spreading 100mg

micro-particulate catalyst substrate on the surface of a 40mm x100 mm sample boat. The

catalyst particles were distributed as a thick layer owing to the size limit of the sample boat.

Since CNTs yield is directly dependent on catalyst surface area, higher yields can be

obtained if the catalyst particle layer is thinned over a larger area.

Table 1. Temperature dependence on yield of CNTs obtained by CVD process

Reaction temperature (°C)	650	700	750	800	900	950	1000	1050
CNT yield (weight %)*	30	177	388	378	689	644	481	235

* Relative yield based on weight of substrate catalyst

The individual tubule structure of linear CNTs can be influenced by reaction temperature in the method of the invention. Figure 8 shows low magnification TEM photomicrographs of the CNTs grown at different temperatures. It is seen that all the CNTs have a "bamboo-like" structure. Inside each CNT the structure is identical along its length, the compartments are spaced at nearly equal distance. The density of the compartments per 100 nm along the tubule axial length was measured from the TEM photomicrographs for CNTs obtained at a reaction temperature of 800°C (Figure 9). It is evident that the compartmental density decreases with the increasing of diameters of the CNTs. The compartmental densities of CNTs grown at different temperatures have similar tubule diameter dependence. The diameters of the CNTs are distributed over a wide range at a single growth temperature and also with different growth temperatures. CNTs grown at 650°C, 750°C, 800°C, 950°C and 1050°C have diameters ranging from 10 to 20 nm, 20 to 54 nm, 20 to 69 nm, 20 to 88 nm, and 60 to 186 nm, respectively. Even though the diameter distribution broadens with the increase of temperature, the diameters of a majority of tubules are distributed over a narrow region at higher reaction temperatures. Since the tubule diameters of the CNTs are mainly determined by the size of the corresponding catalyst

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particles in the CVD process, the increase of CNTs diameter with the temperature indicates that larger catalyst particles are formed at higher growth temperature.

The graphitization (process of forming of planar graphite structure or "graphene layer) of individual tubules and the number of concentric graphene layers comprising the linear CNTs obtained by the present invention can be influenced by reaction temperature. Figure 10 shows high magnification TEM images of CNTs grown at 650°C, 800°C, and 1050°C, respectively. Their outer diameters are approximately 13, 23, and 65 nm, respectively. The number of graphene layers contained within the walls is approximately 12, 24, and 50, respectively, and the graphene layers contained in their diaphragms are 3, 9, and 20, respectively. The number of graphite layers within the CNT wall and the diaphragm of the compartment increase with the temperature. It is evident that the graphitization of the CNTs is significantly improved with the increase of temperature. Unlike CNTs with morphology consisting of concentric cylindrical layers in their walls, those with a "bamboo-like" morphology have parabolic shaped layers stacked regularly along the length. The graphene layers of the bamboo-like CNTs terminate at the surface of the tubes, whereby the edges of the graphene layers are exposed.

In another aspect, the present invention relates to a composition comprising a substrate capable of supporting the growth of CNTs on its surface, containing one or more CNTs with a branched ("Y-shaped") morphology, referred to herein as branched CNTs, wherein the individual arms constituting branched tubules are either symmetrical or unsymmetrical with respect to both arm lengths and the angle between adjacent arms.

In a preferred embodiment, the composition comprises a substrate containing one or more branched CNTs, including 1) a plurality of free standing, branched CNTs attached to

the substrate and extending outwardly from the substrate outer surface, and 2) one or more

CNTs with a branched morphology wherein the CNT tubule structures have Y-junctions with

substantially straight tubular arms and substantially fixed angles between said arms.

As shown in Figure 11, branched CNTs synthesized by the methods of the invention

comprise a plurality of Y-junctions with substantially straight arms extending linearly from

said junctions. The majority of branched CNTs possess Y-junctions having two long arms

that are a few microns long (about 2 to about 10 μm), and a third arm that is shorter (about

0.01 to 2 μm). CNTs with Y-junctions comprising three long arms (up to about 10 μM), and

with multiple branching forming multiple Y-junctions with substantially linear, straight arms

can be also obtained by the method of the invention. High magnification SEM micrograph

(Fig.10b) shows that the branched CNTs of the invention possess Y-junctions that have a

smooth surface and uniform tubule diameter about 2000 nm. The angles between adjacent

arms are close to about 120°, thereby resulting in branched CNTs that have a substantially

symmetric structure. All Y-junctions have a substantially similar structural configuration,

regardless of their varying tubule diameters.

Referring to Figure 12, it is shown for branched CNTs of the invention that most Y-

junctions have hollow cores within their tubular arms (Fig. 12a). A triangular, amorphous

particle is frequently found at the center of the Y-junction (inset in Fig. 12a). Compositional

analysis by an energy dispersive x-ray spectrometry (EDS) indicates that the triangular

particles consist of calcium (Ca), silicon (Si), magnesium (Mg), and oxygen (O). The Ca and

Si are probably initially contained in the catalyst material. It is frequently observed that one

of the two long arms of the Y-junction is capped with a pear-shaped particle (Fig. 12b and

lower inset), that a similar chemical composition as that of the aforementioned triangle-

shaped particle found within the tubules at the Y-junction. A trace amount of cobalt (Co)

from the catalytic material is found at the surface of such pear-shaped particle. The tubule of

the other long arm of the branched CNT (Fig. 12b) is filled with crystalline magnesium oxide

(MgO) from the catalytic material (confirmed by diffraction contrast image in the EDS

spectrograph). Selected area diffraction patterns (upper right inset in Fig.12b) indicate that

one of <110> reflections, [101], of the MgO rod is parallel to [0002] reflection (indicated by

arrow heads) from carbon nanotube walls. Therefore, MgO rod axis is along [210].

Additionally, Y-junctions filled with continuous single crystalline MgO from one arm, across

a joint, to another arm can also be obtained. Figure 12c shows a double Y-junction, wherein

only one arm of the right-side Y-junction is filled with single crystal MgO. Inset in Figure

12b shows a magnified image of the end of the MgO filled arm, illustrating an open tip, that

provides entry of MgO into the CNT Y-junctions. Figure 12d shows a highly magnified

partial Y-junction, which is well graphitized, and consists of about 60 concentric graphite

layers (the graphite layers are only partially shown) in its tubule arms, and a hollow core with

a diameter of about 8.5 nm.

The catalytic substrates constituting the catalyst material for producing branched

CNTs preferably comprise at least one transition metal or metal alloy that is deposited on or

impregnated within a support substrate comprising a metallic or non-metallic oxide.

Transition metals useful in the catalytic substrates of the invention include iron, cobalt,

nickel, or alloys and combinations thereof. Preferred transition metals include iron, cobalt

and nickel. In a most preferred embodiment, the transition metal is cobalt. The metallic or

non-metallic oxide comprising the catalytic substrate of the catalyst material can be either a

transition or a non-transition metallic oxide, or a non-metallic inorganic oxide. Metallic

oxides useful in the catalyst materials include, for example oxides of berylium, magnesium, calcium, strontium and barium. Preferred metallic oxides include magnesium oxide and calcium oxide. In a most preferred embodiment, the metallic oxide is magnesium oxide (MgO). The metallic oxide support substrate of the invention can be either in fused pieces or in a particulate form. Preferred forms for the metallic oxide support includes fused pieces or fused particles (average size from about 0.1 to about 1000 μm). In a preferred embodiment, the metallic oxide support substrate has an average particle size of about 50 μM.

In a preferred embodiment, the catalytic substrate of the invention for producing branched CNTs is prepared by immersing metallic oxide particles, such as for example, magnesium oxide, in an alcoholic metal salt solution, such as for example cobalt nitrate, under conditions sufficient to cause the cobalt to become impregnated into the metallic oxide. The magnesium oxide with impregnated cobalt is filtered, dried and calcined at elevated temperature (preferably about 130°C) for an extended period of time (preferably about 14 hours).

Branched CNTs of the invention can be synthesized in high purity and yield by pyrolysis of a carbon source gas at elevated temperature in the presence of the catalyst material. In a preferred embodiment a carbon source gas, such as for example methane, is pyrolized over the aforementioned catalyst material at a temperature of about 1000°C for about 1 hour. A catalyst gas such as for example, ammonia, hydrogen, nitrogen or mixtures thereof can be additionally introduced into the reaction chamber to provide rapid growth of CNTs.

Linear CNTs produced according to the present invention can be utilized to form composites with other materials, especially dissimilar materials. Suitable dissimilar materials

include metals, ceramics, glasses, polymers, graphite, and mixtures thereof. Such composites may be prepared, for example, by coating the products of the present invention with these dissimilar materials either in a solid particulate form or in a liquid form. A variety of polymers, including thermoplastics and resins can be utilized to form composites with the products of the present invention. Such polymers include, for example polyamides, polyesters, polyethers, polyphenylenes, polysulfones, polyurethanes or epoxy resins.

Branched CNTs of the present invention can find application in construction of nanoelectronic devices and in fiber-reinforced composites. The Y-junction CNT fibers of the invention are expected to provide superior reinforcement to composites compared to linear CNTs.

EXAMPLES

Example 1

Preparation of catalyst substrate for synthesis of linear CNTs

Mesoporous silica containing iron nanoparticles were prepared by a sol-gel process by hydrolysis of tetraethoxysilane (TEOS) in the presence of iron nitrate in aqueous solution by a modification of the method described by Li et al. [*Science, (1996), Vol. 274, 1701-3*]. The catalyst gel was dried to remove excess water and solvents and calcined for 10 hours at 450°C and 10^{-2} torr to give a silica network with substantially uniform pores containing iron oxide nanoparticles that are distributed within. The catalyst gel is then ground into a fine, micro-particulate powder either mechanically using a ball mill or manually with a pestle and mortar. The ground catalyst particles provide particle sizes that range between 0.1 and 100 μM under the grinding conditions.

Example 2

Preparation of catalyst substrate for synthesis of branched CNTs

Magnesium oxide (MgO) supported cobalt (Co) catalysts were prepared by dissolving

0.246g of cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, 98%) in 40 ml ethyl alcohol,

following which immersing 2g of particulate MgO powder (-325 mesh) were added to the

solution with sonication for 50 minutes. The solid residue was filtered, dried and calcined at

$130°C$ for 14 hours.

Example 3

General synthetic procedure for linear CNTs

The synthesis of CNTs is carried out in a quartz tube reactor of a chemical vapor

deposition (CVD) apparatus. For each synthetic run, 100 mg of the micro-particulate catalyst

substrate was spread onto a molybdenum boat (40x 100 mm^2) either mechanically with a

spreader or by spraying. The reactor chamber was then evacuated to 10^{-2} torr, following

which the temperature of the chamber was raised to 750 °C. Gaseous ammonia was

introduced into the chamber at a flow rate of 80 sccm and maintained for 10 minutes,

following which acetylene at a flow rate of 20 sccm was introduced for initiate CNT growth.

The total gas pressure within the reaction chamber was maintained at a fixed value that

ranged from 0.6 torr to 760 torr (depending on desired morphology for the CNTs). The

reaction time was maintained constant at 2 hours for each run. The catalytic substrate

containing attached CNTs were washed with hydrofluoric acid, dried and weighed prior to

characterization.

Example 4

General synthetic procedure for branched CNTs

The MgO supported cobalt catalyst of Example 3 were first reduced at $1000^\circ C$ for 1 hour in a pyrolytic chamber under a flow of a mixture hydrogen (40 sccm) and nitrogen (100 sccm) at a pressure of 200 Torr. The nitrogen gas was subsequently replaced with methane (10 sccm) to initiate CNT growth. The optimum reaction time for producing branched CNTs was 1 hour.

Example 5

Characterization of CNT morphology and purity by Scanning Electron Microscopy (SEM), and tubule structure and diameter by Transmission Electron Microscopy (TEM)

Scanning electron microscopy (SEM) for characterization and verification of CNT morphology and purity was performed on a JEOL JSM-6340F spectrophotometer that was equipped with an energy dispersive x-ray (EDS) accessory. Standard sample preparation and analytical methods were used for the SEM characterization using a JEOL JSM-6340F microscope. SEM micrographs of appropriate magnification were obtained to verify tubule morphology, distribution and purity.

Transmission electron microscopy (TEM) to characterize individual tubule structure and diameter of the CNTs was performed on a JEOL 2010 TEM microscope. Sample specimens for TEM analysis were prepared by mild grinding the CNTs in anhydrous ethanol. A few drops of the ground suspension were placed on a micro-grid covered with a perforated

carbon thin film. Analysis was carried out on a JEOL 2010 microscope. TEM micrographs of appropriate magnification were obtained for determination of tubule structure and diameter.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for this purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention.